

DEVELOPMENT OF A COMPACT,
HIGH-CAPACITY FeS_2 ELECTRODE

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Introduction

High-specific-energy Li-Al/ FeS_2 cells are being developed at Argonne National Laboratory (ANL) for off-peak energy storage batteries in electric-utility networks.¹ Similar cells, but with higher specific power, are also being developed at ANL for electric automobile batteries. The cells have a molten-salt electrolyte such as the LiCl-KCl eutectic (mp, 352°C) and operate at temperatures between 375 and 450°C. These cells have been found² to be superior to earlier lithium/sulfur cells, in which elemental lithium and sulfur were the active materials. The Li-Al/ FeS_2 cells have exhibited stable performance without significant decreases in capacity upon cell cycling and without severe corrosion problems. Engineering-scale Li-Al/ FeS_2 cells (150 A-hr capacity) for the energy-storage application have been described.³ These cells have achieved specific energies of 140 W-hr/kg at the 10-hr rate and cell lifetimes have exceeded 1800 hr.

This paper describes the design and development of the compact, high-performance FeS_2 electrode used in the more recent of the engineering-scale cells. Also discussed is the operation of laboratory-scale cells and the methods used to achieve dimensional control of the FeS_2 electrode. The information gained in the laboratory studies was used for the design of the larger-scale cells. With the improvements in the FeS_2 electrode, significant advances have been made in achieving stable cell capacity with cycling, improving the utilization of the cell reactants, and achieving dimensional stability of the sulfide electrode.

Laboratory-Scale Experiments

Four laboratory-scale cells were operated; the cells were of the design shown in Fig. 1. The positive (FeS_2) electrodes were about 5.7 cm in diameter and had capacities of 12-13 A-hr. The electrode consisted of a bed of finely divided FeS_2 powder encased in a thin layer of zirconia cloth to contain particulates; this structure was, in turn, encased in a basket of molybdenum mesh to provide structural support. The negative electrode was a solid Li-Al alloy that had been electrochemically formed on a substrate of porous aluminum using a method developed at this laboratory.⁴

Iron disulfide power (reagent grade) was purified before use to remove a silicate impurity; this was accomplished by a flotation technique using tetrabromomethane (density, 3.42). The resulting FeS_2 powder was dried and sieved to select a particle size distribution between 80 and 150 μm . This particle

size was chosen to avoid (1) the dimensional instability that would result from the use of a very fine powder ($<50\text{ }\mu\text{m}$) and (2) the decrease in surface area and, hence, a decrease in FeS_2 utilization that would result from the use of a particle size larger than $150\text{ }\mu\text{m}$.

Several materials were tested for use as current collectors, including Armco iron, nickel, and molybdenum. In test cells, both Armco iron and nickel reacted with the sulfide and eventually were severely corroded. Molybdenum showed no reaction with the cell environment and provided long cell lifetimes. The design of the engineering-scale electrode, therefore, included current collectors of molybdenum. It is believed that a current collector of a more common material can be plated with a thin layer of molybdenum to provide the necessary protection from corrosion. Such a procedure would significantly reduce the cost of the current collectors.

Figure 2 shows typical cell voltage patterns during discharge (lower curves) and charge cycles (upper curves); the two stable voltage plateaus are characteristic of this system. These data were taken for a cell having a molybdenum current collector in the FeS_2 electrode after about 50 hr (Cycle 5) and 200 hr (Cycle 25) of operation. No decrease in capacity with cell cycling was observed; utilization of the cell reactants was about 90%. Because the coulombic efficiency was high ($>95\%$) and the cell resistance was low, energy efficiencies between 60 and 80% were achieved.

Another example of the stability of cell capacity cycling can be seen in Fig. 3. In this cell, a capacity greater than 75% of the theoretical was maintained over a period of 200 hr, at which time the cell operation was voluntarily terminated. In a cell that was operated for 500 hr, a capacity density of 0.43 A-hr/cm^2 (90% of theoretical) was achieved, and no decline in capacity occurred over the entire operating period. The energy efficiency was maintained above 70%.

Design of Engineering-Scale FeS_2 Electrode

The design of the positive electrode developed for the engineering-scale cells is shown in Fig. 4; this electrode has a diameter of 12 cm and a capacity of 150 A-hr. The design was selected to minimize the weight required for current collectors and to maximize the utilization of the FeS_2 reactant. The current collector consisted of five layers of lightweight molybdenum expanded mesh (5-mil thickness) which were cut into circular shape, and joined to a center terminal post with a silver-solder brazing.

The current collector was encased in a thin layer of zirconia cloth to retain the finely divided FeS_2 powder ($150\text{ }\mu\text{m}$); the zirconia cloth was, in turn, encased in a lightweight ($\sim 90\text{ g}$) molybdenum expanded mesh basket for a structural backing. This basket consisted of two halves which were sewn together with a molybdenum wire (5 mil). The FeS_2 ($\sim 170\text{ g}$) was poured into the electrode structure through a small opening.

During loading of the FeS_2 , the electrode was vibrated to provide a uniform distribution of FeS_2 within the structure and the desired degree of compactness. Thus, the resulting electrode structure contained a porous bed of FeS_2 with sufficient space allowed for the expansion of the cell reactant and the addition of the necessary amount of electrolyte. (This technique was developed during the course of the laboratory experiments.) Finally, the entire basket structure was enclosed in a boron nitride fabric (not shown in Fig. 4), which served as a separator. With this design, the total weight of the sulfide electrode was only 280 g (total cell weight, ~ 1200 g).

It is believed that the weight of the electrode can be reduced even further by eliminating the zirconia cloth and molybdenum basket; however, a more suitable form of boron nitride fabric is needed for the electrode separator before this can be accomplished. The boron nitride fabric must be of the proper porosity to retain the finely divided FeS_2 and yet allow sufficient passage of electrolyte; the fabric must also have sufficient strength to give good mechanical backing to the electrode.

Conclusions

The experimental results obtained with the compact FeS_2 electrode have been highly promising. With compact design, engineering-scale FeS_2 electrodes have been constructed with theoretical capacities per unit volume of >1 A-hr/cm³. We believe that a Li-Al/ FeS_2 with this type of positive electrode is capable of achieving a specific energy of ~ 180 W-hr/kg. This value exceeds the specific-energy goal for a single cell that has been set in our program to develop a battery for bulk storage of electric energy.

Acknowledgements

The authors gratefully acknowledge the major contribution by Dr. J. E. Battles and Dr. K. M. Myles in examination of materials. Thanks are also extended to J. A. Allen and L. G. Bartholme for preparing the FeS_2 material and cell components, and G. M. Kesser for the editorial assistance on this paper.

This work was conducted under the auspices of the United States Atomic Energy Commission.

References

1. P. A. Nelson *et al.*, "High Performance Batteries for Off-Peak Energy Storage, Progress Report for the Period January 1973-June 1973," USAEC Report ANL-8038, Argonne National Laboratory (March 1974).
2. D. R. Vissers *et al.*, "A Preliminary Investigation of High-Temperature Lithium/Iron Sulfide Secondary Cells," J. Electrochem. Soc. 121, 665 (May 1974).
3. W. J. Walsh *et al.*, "Development of Prototype Lithium/Sulfur Cells for Application to Load-Leveling Devices in Electric Utilities," IECEC Meeting, San Francisco, California (August 1974).
4. N. P. Yao *et al.*, "Solid Lithium-Aluminum Alloy Electrode in High Temperature Secondary Cells," Abstracts, 144th Meeting of the Electrochemical Society, Boston, Mass. (October 1973).

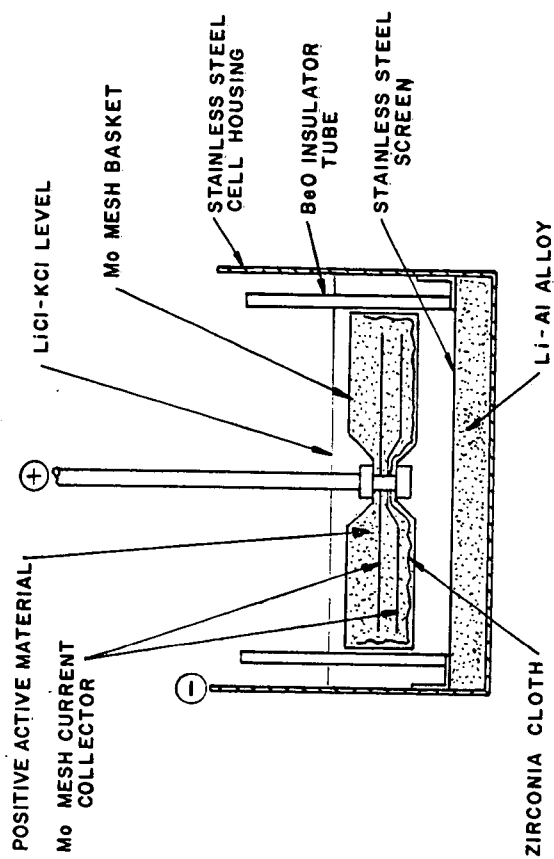


Fig. 1. Laboratory-Scale Li-Al/FeS₂ Cell

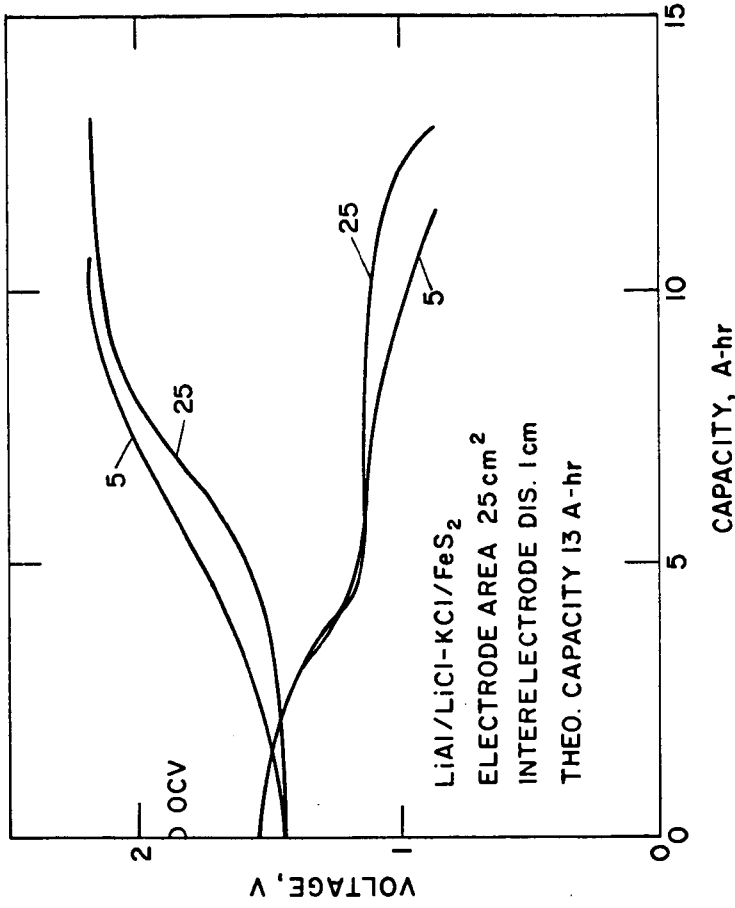


Fig. 2. Typical Measurements of Voltage vs. Capacity in Laboratory-Scale LiAl/FeS₂ Cells

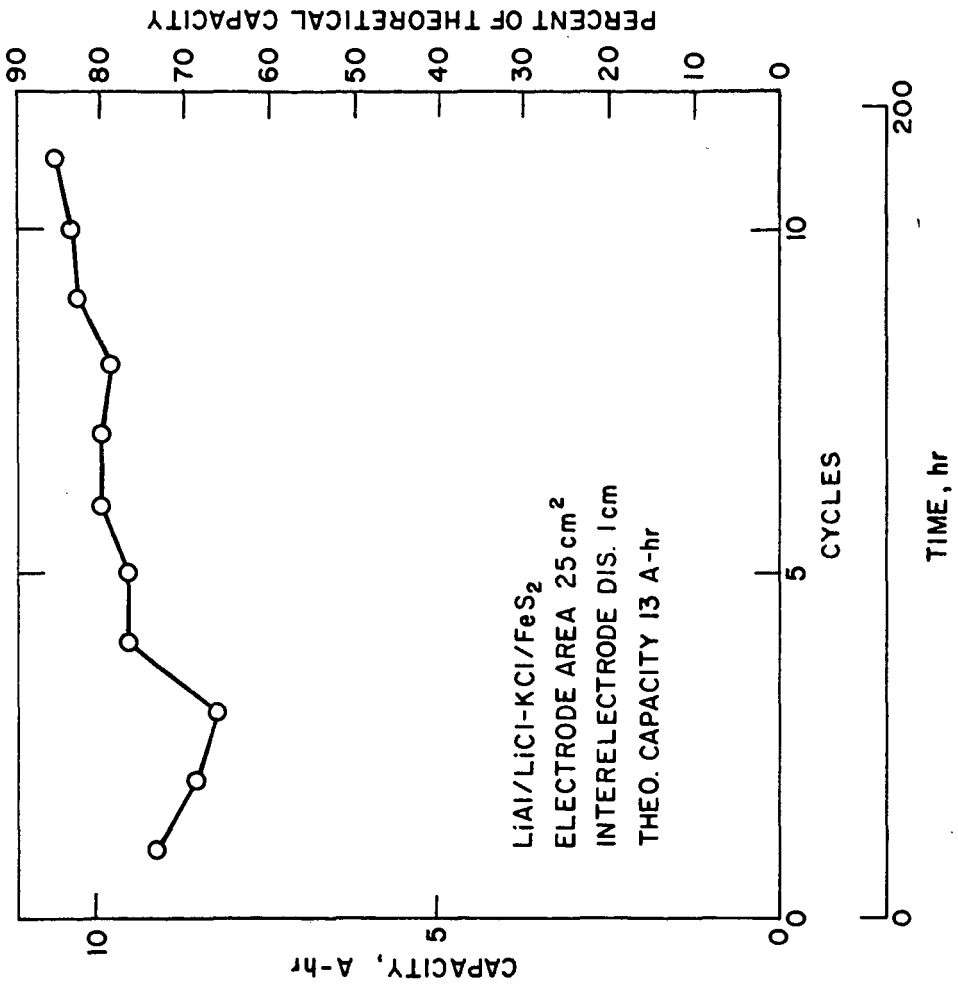


Fig. 3. Capacity of Li-Al/FeS₂ Laboratory-Scale Cell as a Function of Operating Time

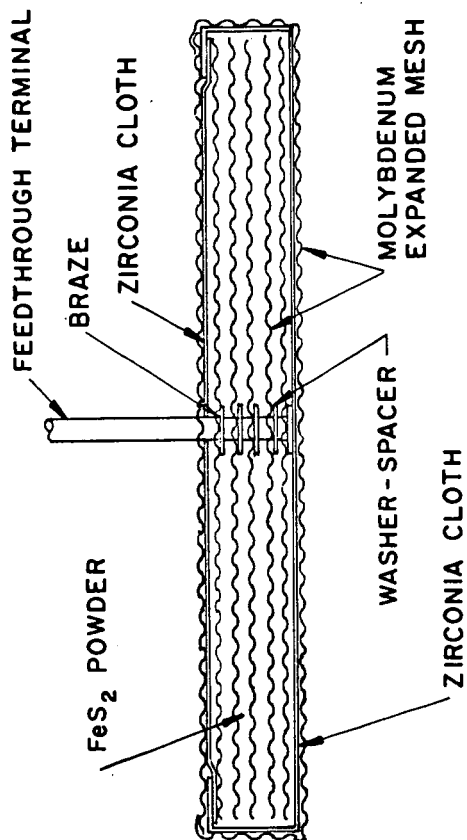


Fig. 4. Design of Engineering-Scale FeS_2 Electrodes